Optimization of SHINE Process: Design and Verification of Plant-Scale AG 1 Anion-Exchange Concentration Column and Titania Sorbent Pretreatment

Nuclear Engineering Division

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by
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ABSTRACT

Argonne National Laboratory has developed a Mo-recovery and -purification system for the shine medical technologies process, which uses a uranyl sulfate solution for the accelerator-driven production of Mo-99. The objective of this effort is to reduce the processing time for the acidification of the Mo-99 product prior to loading onto a concentration column and concentration of the Mo-99 product solution. Two methods were investigated: (1) the replacement of the titania concentration column by an anion-exchange column to decrease processing time and increase the radioiodine-decontamination efficiency and (2) pretreatment of the titania sorbent to improve its effectiveness for the Mo-recovery and -concentration columns. Promising results are reported for both methods.

1. INTRODUCTION

Argonne is assisting SHINE Medical Technologies (SHINE) in their efforts to develop an accelerator-driven process that utilizes a uranyl-sulfate solution for the production of fission Mo-99. The Mo-recovery and -purification system developed at Argonne for the SHINE technology is described elsewhere [CHEMERISOV-2011, STEPINSKI-2013, ROTSCH-2014]. An integral part of the process is a column that separates and recovers Mo-99, followed by a concentration column that reduces the product volume from 15–25 L to <1 L.

Argonne has collected data from batch studies and breakthrough column experiments to utilize the VERSE (Versatile Reaction Separation) simulation program (Purdue University) to design plant-scale chromatographic processes for molybdenum recovery and concentration [STEPINSKI-2012A, YOUKER-2012, STEPINSKI-2012B]. The VERSE model and related simulations were developed by Wang and associates in 1991 [BERNINGER-1991]. Plant-scale column designs were calculated for the separation of Mo from 271 L of a 141 g-U/L uranyl sulfate solution (pH 1) containing 0.0023 mM Mo. In addition, VERSE-designed recovery systems were tested and verified at the laboratory scale in tests using Mo-99 spiked and irradiated uranyl-sulfate solutions, and the results showed that this approach is successful [YOUKER-2012].

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For the full-scale SHINE Mo recovery column, a 14 x 10 cm column utilizing S110 (Sachtopore, TiO_2, normal phase, 110 μm particle size, 60 Å pores) is used to recover Mo. The uranyl-sulfate target solution is passed through the column in the up-flow direction at a flow rate of 2,258 mL/min for 120 min. The loading step is followed by a wash with 10 bed volumes (BV) of 0.1 M H_2SO_4 to remove remaining unadsorbed uranium and fission products from the column. The acid wash is followed by washing the column with 10 BV of water before stripping the Mo in the down-flow direction with alkaline solution. The Mo is removed from titania with hydroxyl ions. Since the first step in the stripping process is the reaction of OH^- with protonated titania sites, the column is pretreated with 3 BV of 1 M NaOH to facilitate the stripping process. This step allows utilization of an overall smaller volume of solution in the stripping process. Subsequently, removal of the Mo product with 20 BV (as discussed in the Mo recovery column stripping section) of 0.1 M NaOH at 5 cm/min and 80°C yields 30.8 L of a 0.020 mM Na_2MoO_4 solution. Because it is compatible with the subsequent product concentration steps, 0.1 M NaOH solution was chosen for the stripping step.

For the 5 L mini-SHINE experiment conducted at the Argonne LINAC facility [CHEMERISOV-2011, STEPINSKI-2013, ROTSCH-2014], a downscaled 2 x 10 cm column was used. The 140 g-U/L uranyl sulfate solution at pH 1, containing 0.0023 mM Mo, was loaded at 40 mL/min and 80°C for 120 min. For Mo stripping, the sorbent was pretreated with 3 BV of 1 M NaOH, followed by 23 BV of 0.1 M NaOH, resulting in 820 mL of Mo product. The product was stripped at 5 cm/min and 80°C. A complete Mo stripping profile was obtained under irradiation conditions.

To reduce the ~30 L volume of Mo-product solution in the SHINE process to less than 1 L for the subsequent LEU Modified Cintichem (LMC) process, a Mo concentration process was developed. The titania sorbent (S40) with 40-micron particle size and 60 Å pore size was chosen as described previously [STEPINSKI-2012B]. In the proposed full-scale process, the Mo-product solution containing 0.025 mM Mo is acidified to pH 2 and loaded onto a S40-packed column (5 x 1 cm) at 410 mL/min for 60 min. The loading step is followed by a wash step using 10 BV of 0.01 M HNO_3 to remove the remaining un-adsorbed impurities from the column. The acid wash is followed by washing with 10 BV of water before stripping Mo with alkaline solution. Subsequently, Mo is removed from the column with 16 BV of 0.1 M NaOH at 5 cm/min (98.2 mL/min) and 70°C.

For the 5 L mini-SHINE experiment conducted at the Argonne LINAC facility, a 1 x 1 cm concentration column design was used. The product solution from the Mo-recovery column, which contained 0.012 mM Mo, was acidified to pH 2 with 10 M HNO_3 and loaded at 16 mL/min for 60 min at 80°C. Molybdenum was stripped from the column with 30 BV of 1 M NaOH at 70°C and 5 cm/min (4 ml/min). In the 5 L mini-SHINE experiment, 30 BV (25 mL) of stripping solution was used to remove Mo from the concentration column due to the large dead volume present in the system (15 mL). High Mo loadings and recoveries for the concentration column process have been shown in tracer and irradiated uranyl sulfate solution experiments [YOUKER-2012].

Discussed below are two studies that were undertaken to optimize the current Mo-recovery and -optimization process. Discussed first is the replacement of the titania concentration column by an anion-exchange column to decrease processing time and increase the radioiodine-decontamination efficiency. Discussed second is means to improve the effectiveness of the titania Mo-recovery and -concentration columns by pretreatment of the titania sorbents.

2. APPROACH

The acidification of the Mo-99 product prior to loading onto a concentration column and concentration of the Mo-99 product solution prior to feeding it to the LMC process add about 3 hours to the total processing time. A loss of 3 hours in processing Mo-99 is significant; about 1% per hour of Mo-99 activity is lost to decay. Therefore, lowering the processing time is important. Because an anion-exchange column adsorbs molybdenum from an alkaline solution and molybdenum is stripped from the column with acid, replacement of the titania sorbent used for the concentration column with an AG 1 anion-exchange resin would provide an acidic feed solution directly for the LMC process, thereby eliminating pH adjustment and evaporation steps. As a consequence, replacement of titania sorbent with AG 1 resin could reduce the processing time by about 3 hours.

The AG 1 resin sorbs MoO_4^{2-}, I^-, and IO_3^- from alkaline media. Replacement of the titania sorbent with the AG 1 resin provides two additional benefits: (1) removing iodine from the Mo product prior to the LMC process and (2) potentially providing a method for recovering a commercial I-131 product. Iodine decontamination is a challenge in the LMC process, and its removal during the prior Mo-product-concentration step would decrease the technical risk of radioiodine contamination of the final Mo product. Because the radioiodine can be recovered from the resin in a separate step following Mo stripping, use of an anion-exchange resin also provides an opportunity to capture and recover I-131 for commercial purposes. Therefore, molybdenum can be removed from the column by using nitric acid, and other iodine species and iodate can be removed during subsequent wash steps. Most of the iodine will remain on the column as iodide and can be subsequently removed with more aggressive stripping agents. This approach is currently used in Argentina, where an anion exchange column is used to recover and purify Mo-99, while I-131 is collected for sale [CESTAU-2006].

We have examined the use of an AG 1 resin for concentrating the Mo-recovery column product from 23.5 L to <1 L [STEPINSKI-2012B]. Organic resins are kinetically superior to inorganic sorbents such as titania and, therefore, can result in shorter mass transfer zones and smaller column designs. The VERSE simulation program was used to design a Mo-concentration column employing AG 1-X8, which is available in analytical grade from Bio-Rad and was selected for adsorbing and concentrating Mo from the Mo-recovery-column strip solution. AG 1 resins are strongly basic anion exchangers capable of exchanging anions of acidic, basic, and neutral salts and ampholytes on the basic side of their isoelectric point. The functionality of the AG 1 resins is provided by quaternary-ammonium functional groups attached to a styrene divinylbenzene copolymer lattice. The high crosslinking of the resins (8% crosslinked) allows sorption, exchange, and separation of low-molecular-weight inorganic anions while offering a higher physical resistance to shrinking and swelling. The hydroxide form was selected as the most activated form. It is thermally stable to 50°C. The 200–400 mesh wet bead size provides high resolution and low spreading of the mass transfer zone, therefore resulting in a smaller column while allowing column designs within a pressure drop (ΔP) constraint of 0.8 atm. Preliminary designs were proposed for loading 23.5 L of Mo-containing 0.1 M NaOH solution on an AG1-X8 packed column in 1 h, while keeping $\Delta P \leq 0.8$ atm.

Column breakthrough and uptake experiments were conducted to confirm process designs, examine experimental results, and determine a process operational envelope.

3. THEORY

3.1 Versatile Reaction-Separation (VERSE) Model and Dimensionless Groups

The VERSE model and related simulations were developed by Wang and associates in 1991 [BERNINGER-1991]. The design method is derived from the analyses of the dimensionless groups in rate model equations. The design is based on intrinsic (or scale-independent) parameters, which include the system parameters (particle porosity and bed void fraction), adsorption isotherms, Brownian diffusivities, intra-particle pore diffusivities, and other mass transfer parameters (axial dispersion coefficient and film mass transfer coefficient). To calculate column profiles and frontal data, the general VERSE model takes into account detailed mass-transfer effects (axial dispersion, film mass transfer, and intra-particle pore and surface diffusion), slow adsorption and desorption [WHITLEY-1993], and possible chemical reactions in the mobile phase or in the solid phase during the separations [VAN COTT-1991, WHITLEY-1994, YU- 2006, TSUI- 2012]. Although the general VERSE model can take into account parallel intra-particle pore and surface diffusion, previous studies have shown that at a relatively low concentration region, effects of surface diffusion on frontal or elution chromatography cannot be distinguished from those of pore diffusion. As a result, a pore-diffusion model can be used to predict closely the frontal curves [MA-1996, CHUNG-2010]. Since the Mo feed concentration in the system of interest is relatively low (~10^{-2} mM), the pore-diffusion model was tested for process simulation and design. The assumptions and equations for the pore-diffusion VERSE model have been reported elsewhere [BERNINGER-1991].

3.2 Langmuir Adsorption Isotherm Model

When adsorption and desorption rates are much higher than the mass transfer rates, the concentrations in the solid and solution phases are at equilibrium. Under such conditions, the local solid-phase concentrations are related to the local solution-phase concentrations by an equilibrium isotherm at a given temperature. The Langmuir adsorption isotherm equation used in this study is:

$$q = \frac{aC}{1+bC}$$

(1)

where a and b are the Langmuir isotherm parameters for adsorbing species, and q is the solid-phase concentration of species adsorbed in equilibrium with the solution phase concentration C. If bC~1 or bC>>1, the relation between q and C is nonlinear, and the concentration is defined to be in the nonlinear isotherm region. If bC<<1, q $\approx$ aC, the concentration in the solution is in the linear isotherm region.

3.3 Constant Pressure-Limit Line

In addition to the loading time and breakthrough limit requirements, a pressure-drop limit is also considered in the column design. The column pressure drop can be estimated from the Ergun equation:

$$\Delta P = L \times \left[150 \frac{(1-\varepsilon_b)^2}{\varepsilon_b^{\,3}} \frac{\mu u_s}{4R^2} + 1.75 \frac{(1-\varepsilon_b)}{\varepsilon_b^{\,3}} \frac{\rho u_s^{\,2}}{2R} \right]$$

(2)

where ΔP is the pressure drop of the column packing, μ is the viscosity of the mobile phase, and ρ is the density of the mobile phase, ε_b is the inter-particle void fraction, u_s is the superficial velocity, R is the radius of sorbent particle, L is the column packing length.

4. EXPERIMENTAL

4.1 Materials

Nitric acid (70%, Sigma Aldrich) and sodium hydroxide (96%, Sigma Aldrich) were used as received. Stable Mo was added as sodium molybdate, also from Sigma Aldrich. Molybdenum-99 was milked from a 1 Ci Tc-99m generator (Lantheus Medical Imaging, N. Billerica, MA) using 1.0 M NH$_4$OH. The resin AG 1-X8 was obtained from Bio-Rad (Hercules, CA) and was used as the sorbent for Mo adsorption.

4.2 Batch Equilibrium Tests

To determine the uptake of Mo as a function of Mo concentration, 1 mL stable Mo in a sodium hydroxide solution spiked with Mo-99 was contacted with a known amount (10 ± 1 mg) of sorbent for 0.5 hours. This step was accomplished with a vortex mixer at room temperature or a thermostated shaker bath. After equilibration, the solution was withdrawn and filtered by a syringe fitted with a polyvinylidene fluoride membrane filter having a 0.22-µm pore size (Millipore). Blank experiments showed that the filter does not uptake Mo-99. The Mo concentration in the solid phase in equilibrium with the final concentration in the solution can be calculated as follows:

$$q=\frac{(C_o-C_s)V}{W}\rho_{packing}$$

(3)

where C_o is the initial Mo concentration in the solution, C_s is the final Mo concentration in the solution, and q is the Mo concentration in the solid phase in equilibrium with the final concentration in the solution. Also, V is the volume of the solution, W is the mass of dry sorbent, and $\rho_{packing}$ is the packing density of the sorbent, which is defined as the ratio of the sorbent dry weight to the packing volume. The unit for q is mmol/L packing volume. For AG 1-X8, the packing density ($\rho_{packing}$) was determined to be 990 g/L.

4.3 Column Tests

Breakthrough tests were used to estimate Mo intra-particle diffusivity and to verify the Langmuir isotherm parameters. A solution containing 0.2 mM Mo as Na$_2$MoO$_4$ and tracer Mo-99 in 0.1 M NaOH was loaded in the up-flow direction at room temperature and 48.3 cm/min on an AG 1-X8-packed Omnifit Benchmark column (0.66 cm ID × 1 cm long), using an ÄKTA LC System. The column was pre-equilibrated with 10 column volumes of 0.1 M NaOH. The column was loaded with 1600 mL of solution, and the effluent was collected in 13-mL fractions, which were sampled and gamma counted.

Column design verification utilizing tracer Mo-99 was conducted in a laboratory-scale column (0.66 cm ID x 3.5 cm long) packed with AG 1-X8. The feed solution, which contained

0.0234 mM Mo in 0.1 M NaOH, was loaded in the up-flow direction at 14 ml/min (41 cm/min) for 60 min at room temperature. This loading was followed by washing with 10 BV of 0.1 M NaOH and 10 BV of water. Product was stripped using 1 M HNO_3 at 5 cm/min.

4.4 Column Design Demonstration Using LINAC-Irradiated Target Solution

Five liters of a 149 g-U/L (grams of uranium per liter of solution) uranyl sulfate (pH=1 and 19.8% [235]U) solution containing 0.002 mM Mo was irradiated in an electron LINAC at 35 MeV/10 kW power on a Ta target. At the end of bombardment, 110 mCi of Mo-99 was produced. The irradiated uranyl-sulfate solution was loaded on a stainless steel Mo-recovery column (2 x 10 cm) packed with S110 and pre-equilibrated with pH 1 sulfuric acid at 80°C. All loading, washing, and stripping steps were done at 80°C and 40 mL/min. The column was stripped with 100 ml of 1 M NaOH and 790 mL of 0.1 M NaOH. After the Mo recovery, the Mo product was transferred directly through a transfer line to a hot cell for product concentration and purification. An Omnifit BenchMark column (1 x 2 cm) packed with AG 1-X8 was pre-equilibrated with 0.1 M NaOH and subsequently loaded with 820 mL of Mo product solution at 16 mL/min in the up-flow direction at room temperature. The column was washed with 10 BV of 0.1 M NaOH and 10 BV of water. The Mo product was stripped from the column using 1 M HNO_3 in the down-flow direction at room temperature and 5 cm/min (4 mL/min). The concentration-column separation system included an FMI pump; Swagelok 3-, 4-, and 5-way switching valves; and Hamilton 3-port flow valves with a T-plug to direct process streams. This system was operated by using hot cell manipulators. The Mo product solution was purified using LEU Modified Cintichem.

4.5 Gamma Counting

The amount of activity in the aqueous samples containing tracer Mo-99 was determined with a Perkin Elmer 1480 Wizard 3-inch NaI Gamma Counter in the 700–900 keV window. Activity in the irradiated samples was determined by using a high-purity germanium detector (HPGe, calibrated with an Eckert & Ziegler mixed isotope standard) connected to an ORTEC DSPEC 50 digital analyzer. These resulting data were analyzed with GammaVision software. The activity in each sample was corrected for decay.

5. RESULTS AND DISCUSSION

5.1 Langmuir Isotherm Parameters

The isotherm data for Mo were obtained via batch adsorption equilibrium tests. The Langmuir isotherm model was applied to fit the data using the nonlinear analysis tool of Origin 2015 (Figure 1). The best fit for uptake of Mo on AG 1-X8 in 0.1 M NaOH at room temperature indicates that the Langmuir "a" = 6365 L solution volume/L packing volume, and "b" = 9.59 mM^{-1}.
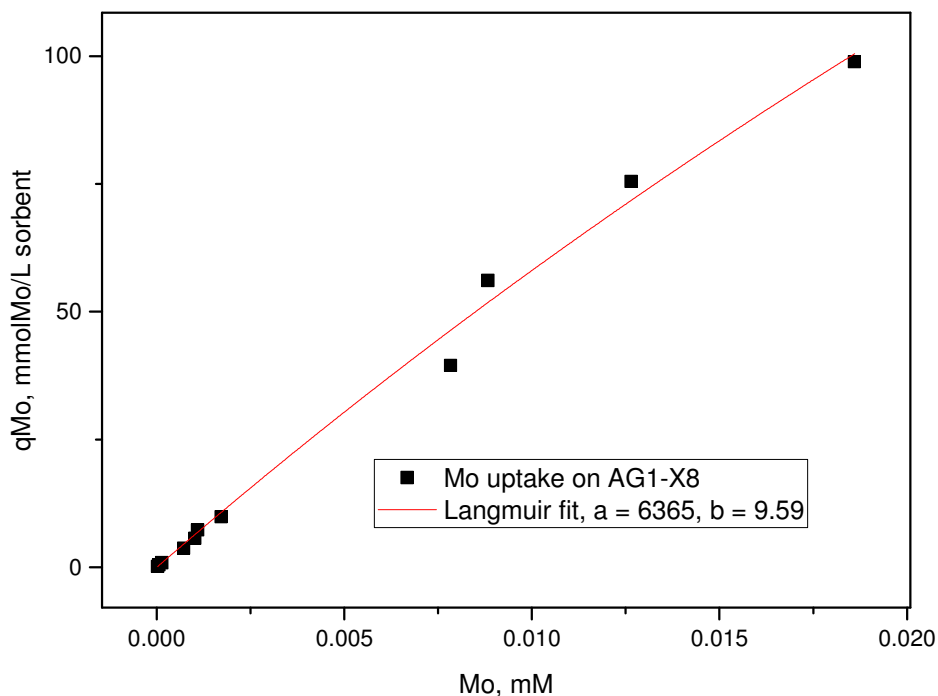
Figure 1. Adsorption isotherm of Mo on AG 1-X8 in 0.1 M NaOH at room temperature.

Uptake of Mo on AG1-X8 was also measured at 50°C and 80°C (Figure 2). The data indicate that the uptake is lower at higher temperatures: at 50°C the Langmuir "a" = 2714 L solution volume/L packing volume and "b" = 4.97 mM^{-1}, whereas at 80°C "a" = 1040 L solution volume/L packing volume and "b" = 1.06 mM^{-1}. The sorbent capacity values for the process feed, where C_f = 0.02 mM Mo, are q_f = 49.4 mmol Mo/L CV at 50°C and q_f = 20.4 mmol Mo/L CV at 80°C. The sorbent capacity values at these higher temperatures are significantly lower than that at room temperature (q_f = 107 mmol Mo/L CV for C_f = 0.02 mM Mo).
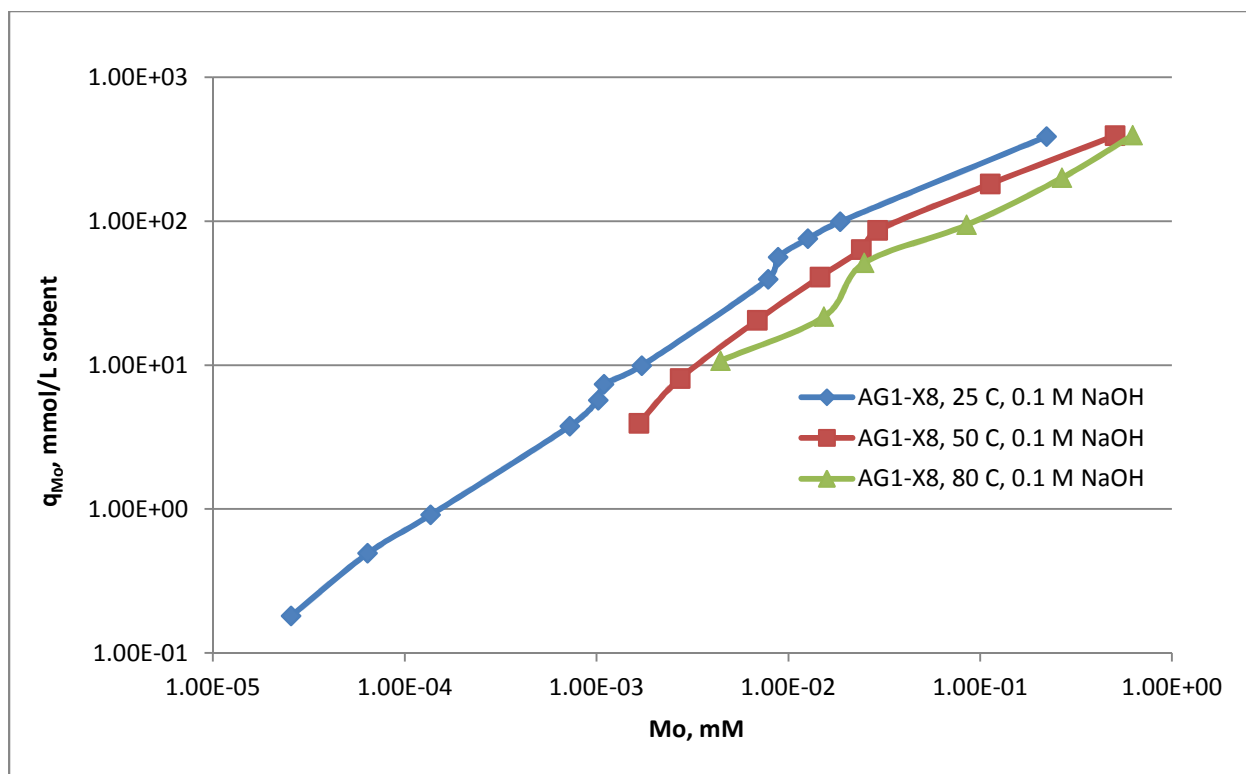
Figure 2. Adsorption isotherms of Mo on AG 1-X8 in 0.1 M NaOH at 25°C, 50°C, and 80°C.

Uptake of Mo on AG 1-X8 was also measured at higher OH^- concentrations and room temperature, as shown in Figure 3. The data indicate that the uptake is lower at higher OH^- concentrations. In 0.2 M NaOH, the Langmuir "a" = 1036 L solution volume/L packing volume and "b" = 1.16 mM^{-1}. In 1 M NaOH, "a" = 223.2 L solution volume/L packing volume and "b" = 0.347 mM^{-1}. The sorbent capacity values for the process feed, where C_f = 0.02 mM Mo, are q_f = 20.3 Mo/L CV in 0.2 M NaOH and q_f = 4.40 mmol Mo/L CV in 1 M NaOH. The AG 1-X8 sorbent capacity values at higher OH^- concentrations are significantly lower than that in 0.1 M NaOH (q_f = 107 mmol Mo/L CV for C_f = 0.02 mM Mo).

Uptake of Mo on AG 1-X8 from NaOH solutions was measured with tracer-level Mo-99 as a function of OH^- concentration, as shown in Figure 4. The log-log plot of $[OH^-]$ vs. K_d for Mo-99 has a slope of -2, indicating that 2 OH^- molecules compete with Mo for adsorption. The slope is consistent with the presence of MoO_4^{2-} species in basic solution, where two hydroxide molecules complete with Mo for uptake on AG 1-X8.
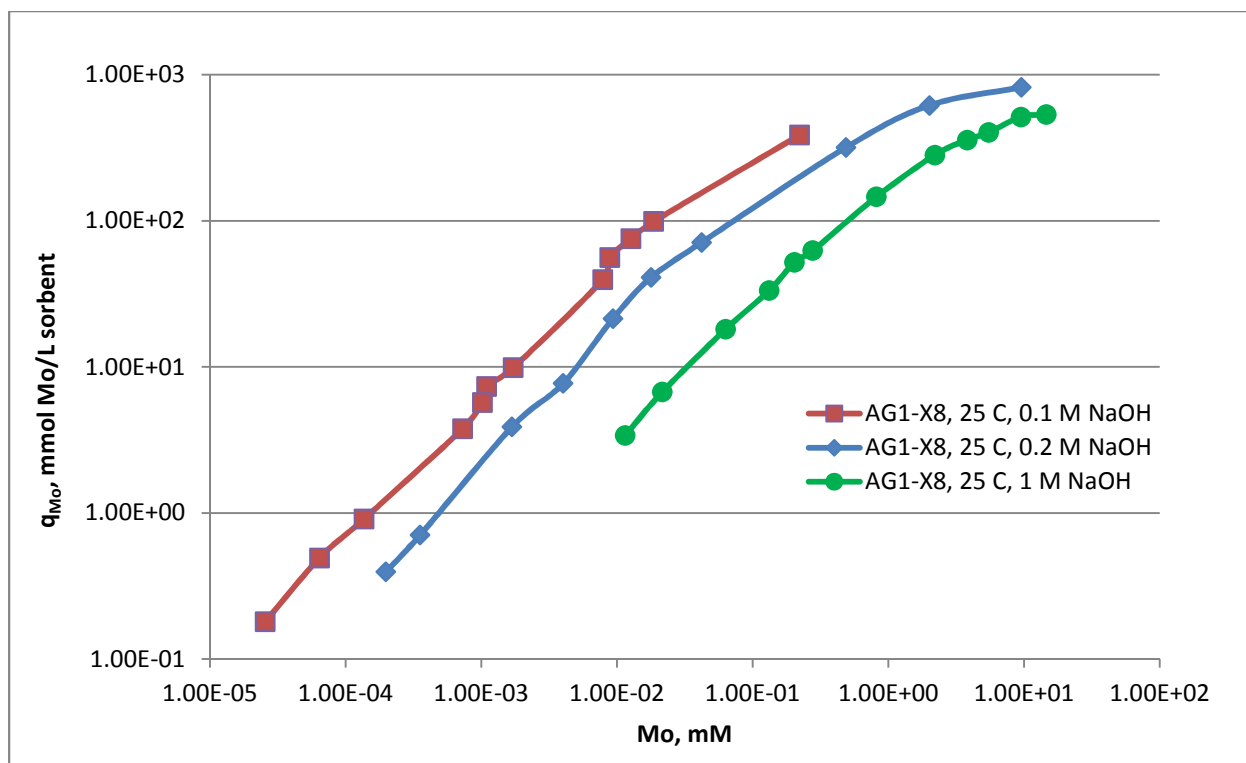
Figure 3. Adsorption isotherms of Mo on AG 1-X8 in 0.1, 0.2, and 1 M NaOH at room temperature.
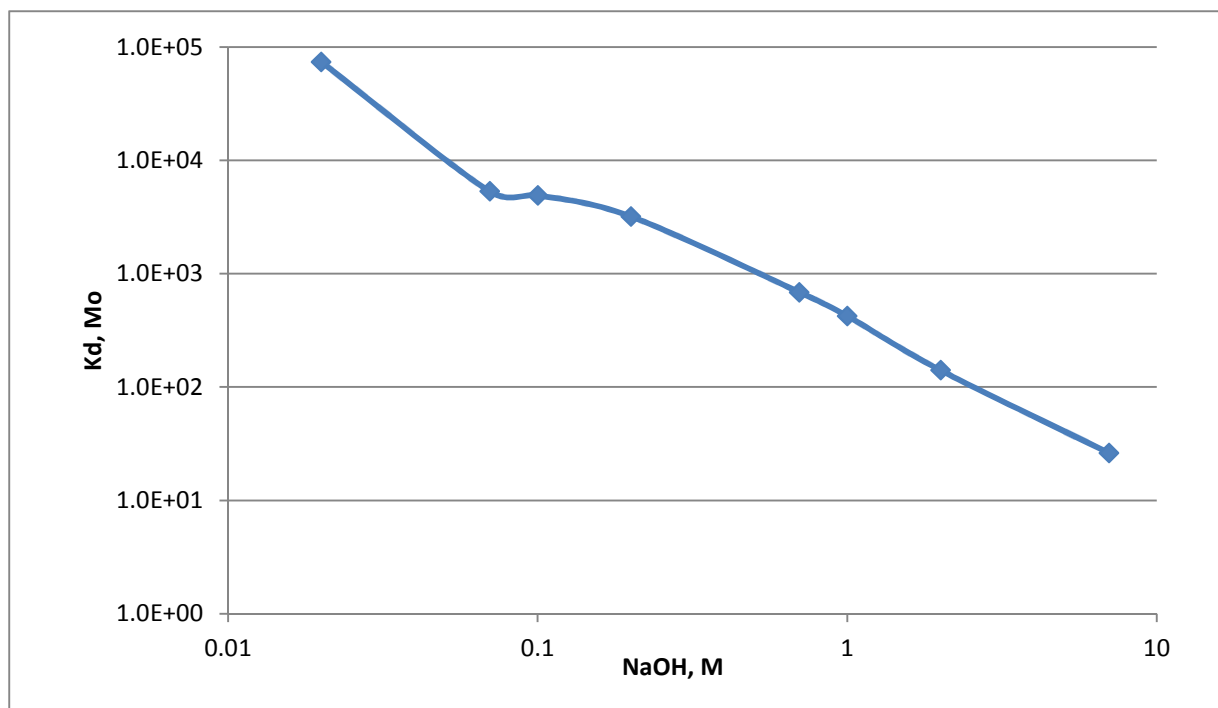
Figure 4. Distribution ratio (K_d) for Mo-99 as a function of OH^- concentration on AG 1-X8.

5.2 Intra-particle Diffusivity

An experiment was performed to estimate D_p and Mo capacity from the breakthrough curve (Figure 5). The breakthrough curve was obtained by loading 1.6 L of 0.2 mM Mo in a 0.1 M NaOH solution on an AG 1-X8 column (0.66 x 1 cm) at 15 mL/min (48 cm/min). The Mo capacity of the sorbent was estimated from the experiment using equation (4),

$$a = \frac{q_f}{C_f} = \frac{C_f \, V_{center}}{V_{column} \, C_f} = \frac{V_{center}}{V_{column}} \tag{4}$$

where V_{center} is the center of the breakthrough curve , V_{column} is the volume of the column, q_f is the amount of Mo adsorbed per packing volume of sorbent (mmol/L CV), and C_f is the Mo concentration in the feed solution (mM). In this experiment, V_{center} is 728 mL, a = 2364 L solution volume/L packing volume, and q_f = 426 mmol/L CV. These sorbent capacity values are in agreement with capacity values obtained from batch studies in Figure 1, where q_f = 436 mmol/L CV for C_f = 0.2 mM.
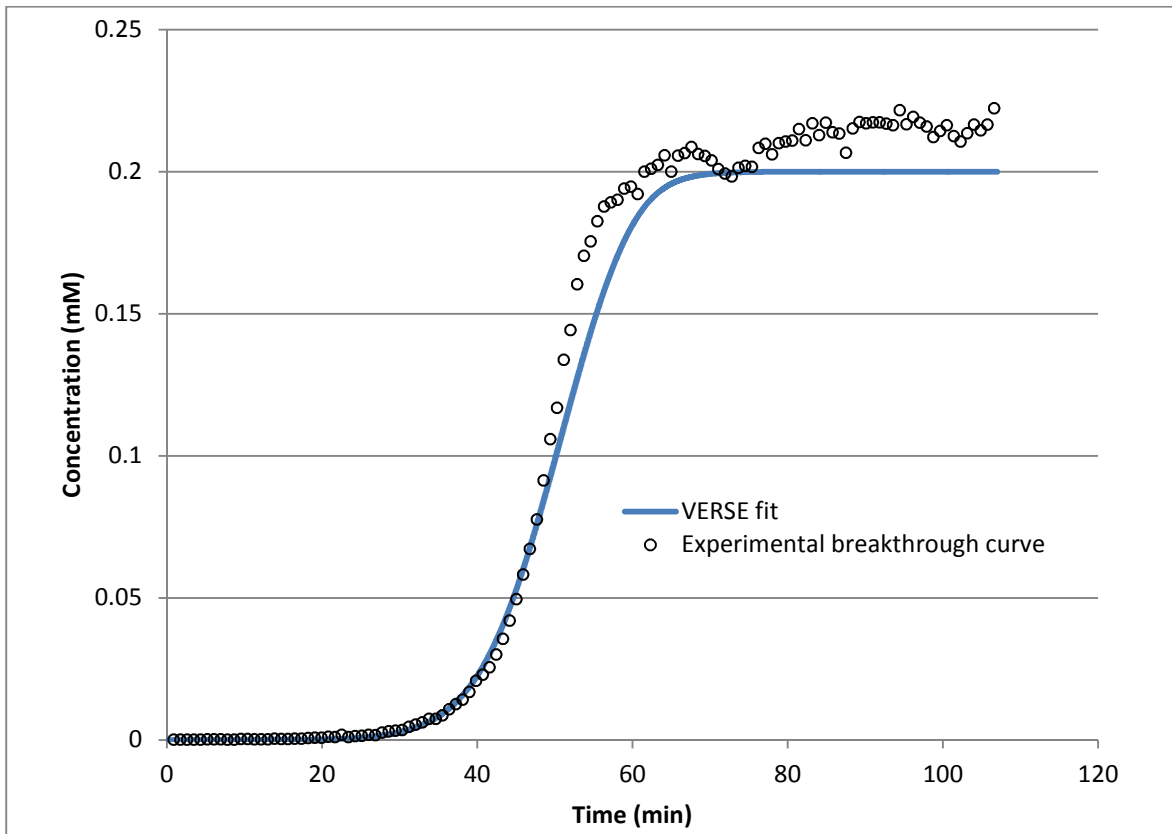
Figure 5. Breakthrough curve for loading 0.2 mM Mo in 0.1 M NaOH on AG 1-X8 packed column (0.66 x 1 cm) at 48.3 cm/min.

The Mo intra-particle diffusivity was estimated by fitting the experimental Mo breakthrough curve with VERSE simulations (Figure 5). The best fit indicates that in 0.1 M NaOH, the Mo intra-particle diffusivity on AG 1-X8 approaches the Mo solution diffusivity value of 8.3 x 10^{-4} cm^2/min.

The agreement between the experimental breakthrough curve and model prediction indicates that (1) the adsorption of Mo in 0.1 M NaOH can be described by the Langmuir isotherm, and (2) the numerical parameters and the intrinsic model parameters (including void fractions, isotherm parameters, and mass transfer parameters) are sufficiently accurate to predict the Mo breakthrough curves in 0.1 M NaOH solution. The intrinsic parameters, system parameters, and numerical parameters used in the VERSE simulations are summarized in Table 1. Where R is the radius of sorbent particle, ε_b is the inter-particle void fraction, ε_p is the intra-particle void fraction, D_b is the Brownian diffusivity, D_p is the intra-particle pore diffusivity, k_f is the film mass transfer coefficient, E_b is the axial dispersion coefficient, $\Delta\Theta_{max}$ is the maximum time step.

Table 1. Parameters used in VERSE simulations.

System Parameters			
Sorbent	R (µm)	ε_b	ε_p
AG 1-X8	20	0.30	0.45
Mass Transfer Parameters			
D_b (cm^2/min)	D_p (cm^2/min)	k_f (cm/min)	E_b (cm^2/min)
8.3 x 10^{-4}	8.3 x 10^{-4}	From Wilson and Geankoplis (1966)	From Chung and Wen (1968)
Isotherm Parameters (Langmuir)			
a (L solution volume/L packing volume)		b (1/mM)	
6365		9.59	

Numerical Parameters					
Axial Elements	$\Delta\Theta_{max}$	Collocation Points		Tolerance	
		Axial	Particle	Absolute (mM)	Relative
50	0.01	4	4	2 x 10^{-5}	10^{-3}

5.3 Column Design Testing

5.3.1 Tracer Experiment

The AG 1-X8 concentration column design was successfully tested with a feed solution containing 0.1 M NaOH, 0.0234 mM Mo, and tracer Mo-99. The results indicate that 99.9+% of Mo was loaded on the column and 99.9+% of Mo was stripped with 1 M HNO_3 in 30 BVs. An insignificant amount of Mo-99 was found in the first 11.5 BVs of the 1 M HNO_3 strip solution and 99.9+% of Mo was found in the subsequent 20 BVs.

5.3.2 Mini-SHINE Experiment

5.3.2.1 Stripping of the Mo-Recovery Column

In the mini-SHINE experiment, Mo is removed from titania using an alkaline solution. Since the first step in the stripping process is the reaction of OH⁻ with protonated titania sites, the S110 recovery column was pretreated with ~3 BV of 1 M NaOH to facilitate the stripping process (Figure 6). This step allows utilization of an overall smaller volume of solution in the stripping process. Subsequently, the Mo product is removed with 0.1 M NaOH at 5 cm/min. The stripping profile from the Mo-recovery column loaded from the irradiated target solution in the mini-SHINE experiment (Figure 6) indicates that a large amount of the Mo is present in the second portion of the 1 M NaOH prewash, 1.6-3 BV. In the current SHINE process, the Mo product from the S110 recovery column is acidified to pH 2 prior to loading on a S40 titania concentration column. The presence of 1 M NaOH in the Mo product solution does not impact the S40 titania concentration column, as the feed solution is acidified to pH 2 prior to loading. Therefore, to keep the stripping process as short as possible and limit the amount of waste, it is recommended that 3 BVs of 1 M NaOH prewash and 17 BVs of 0.1 M NaOH strip solution be collected together, acidified to pH 2, and loaded on the S40 titania concentration column.
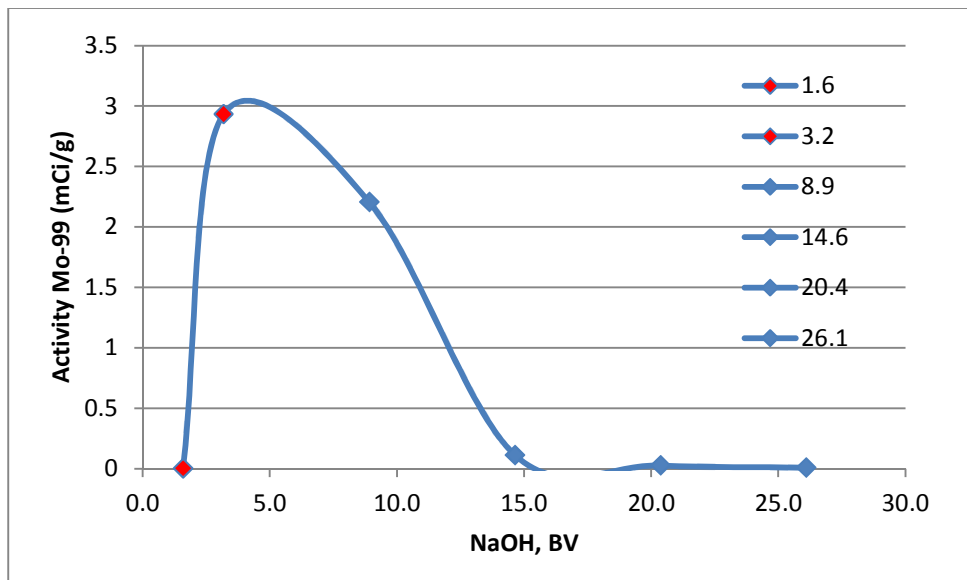
Figure 6. Molybdenum stripping profile at 5 cm/min for S110 recovery column loaded with LINAC irradiated uranyl sulfate solution. First 3 BVs are 1 M NaOH, and the remaining BVs are 0.1 M NaOH.

5.3.2.2 Anion-Exchange Concentration Column

stripped in a two-step process with 100 mL of 1 M NaOH, and Mo product was recovered with 720 mL of 0.1 M NaOH. This solution was loaded on an AG 1-X8 packed column (1 x 2 cm) at 16 mL/min (20 cm/min) and room temperature. Unexpectedly, 80% of Mo

was not captured and found in the eluent. The low capture of Mo on AG 1-X8 column was most likely due to combining the 1 M NaOH prewash solution with the 0.1 M NaOH strip in the S110 recovery column strip, resulting in ~0.21 M OH$^-$ in the Mo product solution. The Mo capacity on
AG 1-X8 in 0.2 M NaOH is five times lower than that in 0.1 M NaOH. The experiment was also plagued by column clogging, which was most likely caused by residual uranium present in the dead volumes prior to stripping of the Mo-recovery column. The gamma counting results for the recovery column, concentration column and LEU Modified Cintichem processes are included in Appendix 1.

Because of the adverse effect of higher NaOH concentration on the anion-exchange sorbent capacity, the two-step stripping process using 1 M NaOH prior to Mo stripping with 0.1 M NaOH is not recommended when an AG1-X8 concentration column is used. Instead, it is recommended to strip the recovery column in a single step with 20 BVs of 0.1 M NaOH. The initial 5 BVs of 0.1 NaOH strip solution is not expected to contain Mo-99 and can be collected separately as waste.

5.4 Column Designs

Based on the updated intrinsic parameters, column designs utilizing AG 1-X8 were developed for concentrating the Mo product from the Mo-recovery column. The feed solution for the plant-scale concentration column is 30.8 L of 0.02 mM Mo in 0.1 M NaOH, which will be loaded in 1 h. The density and viscosity of a 0.1 M NaOH solution at 25°C were assumed to be the same as that of water: 0.997 g/mL and 0.89 cP, respectively. The intrinsic parameters, system parameters, and numerical parameters used in VERSE simulations are summarized in Table 1. Table 2 presents three possible concentration column configurations. Column lengths were chosen by rounding up the mass transfer zone (MTZ) length to the nearest 0.5 cm. The recommended design is a 4 x 1.5 cm column loaded for 60 min at 41 cm/min. After washing with 10 BVs of 0.1 M NaOH and 10 BVs of water, the column should be pretreated with 10 BVs of 1 M HNO$_3$, which is not expected to contain Mo-99 and should be collected as waste. Subsequently, Mo-99 should be stripped with 20 BVs of 1 M HNO$_3$, resulting in ~ 390 mL of Mo feed for the LMC purification process.

Table 2. Possible concentration column configurations.

Column ID (cm)	Velocity (cm/min)	MTZ0.1% (cm)	Column length (cm)	Column volume (mL)	Sorbent weight (g)	ΔP (atm)	Strip volume (mL)
3.5	53.35	1.62	2.00	19	19	0.56	384.8
4	40.85	1.27	1.50	19	19	0.32	377.0
5	26.14	0.85	1.00	20	19	0.14	392.7

5.5 Pretreatment of Titania

During the first phase of the mini-SHINE experiments, a precipitate was observed in the Mo-product solution from the titania Mo-recovery column. The precipitate dissolved during an acidification step using nitric acid prior to loading on the titania concentration column. Inductively coupled mass spectrometry (ICPMS) analyses of the dissolved precipitate showed that it contained mainly uranium and a small amount of silicon. Uranium was found in the Mo-product solution, most likely due to hold-up of uranyl sulfate solution in the mini-SHINE system rather than poor column performance.

In the second phase of the mini-SHINE experiments, separate pumps and flow paths will be used for the acidic solutions, including uranyl-sulfate target solution, and basic solutions to help prevent contamination of uranium in the Mo-product solution from the extraction column. Silicon leaches from the titania sorbent (Sachtopore NP 110) used for the extraction and concentration columns. As a consequence, the titania sorbent was washed with different acidic and basic solutions in an attempt to remove the silicon prior to column packing and testing. The selection of acid and base was based on the mini-SHINE process, where pH 1 sulfuric acid is used to condition the columns, and sodium hydroxide is used to strip Mo from the columns. The ICPMS results indicated that silicon was present in the sulfuric acid and sodium hydroxide solutions used to wash the titania sorbent. Results also showed that 0.5 M sulfuric acid is the most effective solution to remove silicon from the TiO_2 beads (Table 3), although it removes some titanium along with silicon.

In the mini-SHINE process, the acid and base solutions are passed through the TiO_2 packed columns at 80°C. Therefore, the effect of high temperature solutions on the beads was investigated. Table 4 shows that 0.1 M NaOH does not remove silicon and titanium from the beads at elevated temperatures. However, 0.05 M sulfuric acid does remove silicon from the beads without removing any titanium. This observation suggests that the silicon present in the Mo-product solution from the extraction column may be removed by pre-washing the sorbent with high temperature sulfuric acid prior to column packing and testing.

Table 3. Washing the TiO_2 sorbent with sulfuric acid and sodium hydroxide.

TiO_2 beads (g)	Wash Solution	Solution (mL)	Contact time (min)	Temp. (°C)	Mixing	Washed off (mg/g sorbent)	
						Si	Ti
10.08	0.1 M NaOH	25	20	23	Occasional stirring	0.0011	0.0015
10.03	0.5 M NaOH	25	20	23	Occasional stirring	0.0039	0.0005
10.05	1 M NaOH	25	20	23	Occasional stirring	0.0065	0.0003
10.05	0.05 M H_2SO_4	25	20	23	Occasional stirring	0.0146	0.0003
10.03	0.1 M H_2SO_4	25	20	23	Occasional stirring	0.1050	0.0009
10.08	0.5 M H_2SO_4	25	20	23	Occasional stirring	0.2240	0.0943

Table 4. Effect of high temperature washing using 0.05 M H_2SO_4 and 0.1 M NaOH.

TiO2 beads (g)	Solution	Solution (mL)	Contact time at 80-90 °C (min)	Temperature (°C)	Mixing	Washed off (mg/g sorbent)	
						Si	Ti
10	0.1 M NaOH	50	20	80-90	Overhead stirring	NS*	NS
Same bead	0.1 M NaOH	50	20	80-90	Overhead stirring	NS	NS
Same bead	0.1 M NaOH	50	20	80-90	Overhead stirring	NS	NS
Same bead	0.1 M NaOH	50	20	80-90	Overhead stirring	NS	NS
Same bead	0.1 M NaOH	50	20	80-90	Overhead stirring	NS	NS
10	0.05 M H_2SO_4	50	20	80-90	Overhead stirring	0.1445	NS
Same bead	0.05 M H_2SO_4	50	20	80-90	Overhead stirring	0.0947	NS
Same bead	0.05 M H_2SO_4	50	20	80-90	Overhead stirring	0.0811	NS
Same bead	0.05 M H_2SO_4	50	20	80-90	Overhead stirring	0.0545	NS
Same bead	0.05 M H_2SO_4	50	20	80-90	Overhead stirring	0.0378	NS

*NS = not significant.

The results of various contact times with the sorbent and wash solutions show that beyond 20 min the removal of silicon is not significant (Table 5). These results are consistent with previous experiments, where 0.5 M H_2SO_4 removes some titanium, and 0.05 M H_2SO_4 does not remove any titanium.

Table 5. Effect of washing time duration.

TiO2 beads (g)	Solution	Solution (mL)	Contact time (min)	Contact time at 80°C (min)	Mixing	Washed off (mg/g sorbent)	
						Si	Ti
20	0.05 M H_2SO_4	100	50	20	Magnetic stirring	0.0948	NS
20	0.05 M H_2SO_4	100	90	60	Magnetic stirring	0.1175	NS
20	0.05 M H_2SO_4	100	180	150	Magnetic stirring	0.1145	NS
20	0.5 M H_2SO_4	100	20	20 min at RT*	Magnetic stirring	0.2200	0.1670
20	0.5 M H_2SO_4	100	60	60 min at RT	Magnetic stirring	0.2500	0.2110
20	0.5 M H_2SO_4	100	150	150 min at RT	Magnetic stirring	0.2560	0.2065

*RT = room temperature.

As shown by the ICPMS results, 0.5 M H_2SO_4 is the most effective solution to remove silicon from the beads while 0.05 M H_2SO_4 removes silicon without removing titanium. Using these solutions, successive washing experiments have been performed to yield the maximum amount of silicon removed from the beads. Figure 7 shows that two successive washes using 0.5 M H_2SO_4 removed ~83% silicon, and after a fourth wash, little to no additional silicon was removed. Similarly, 0.05 M H_2SO_4 removed almost the same amount of silicon without removing any titanium.
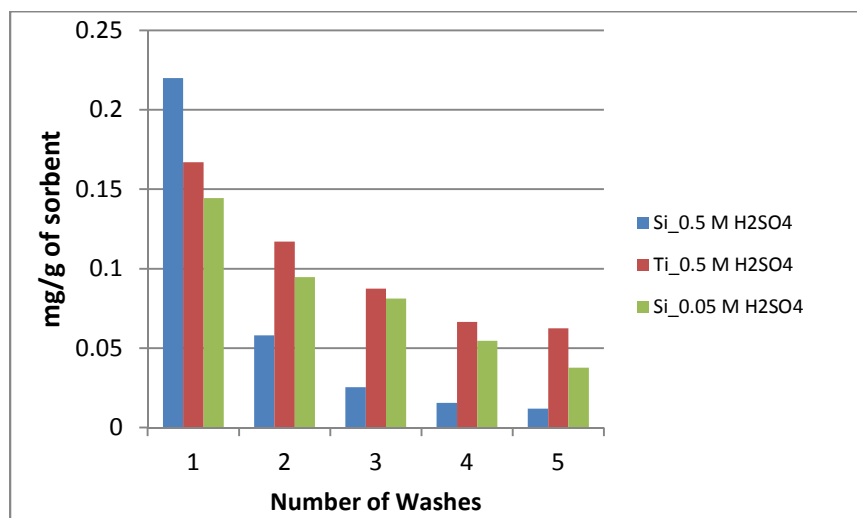
Figure 7. Successive washing of TiO_2 sorbent using 0.5 and 0.05 M H_2SO_4. Washing conditions: ratio of beads to solution, 1:5; contact time, 20 min; overhead stirring; temperature, 23°C for 0.05 M H_2SO_4 and 80–90°C for 0.05 H_2SO_4

The Mo-adsorption performance of the sorbent was determined from the partition coefficient, K_d for molybdenum using pre-treated beads after five successive washes with 0.5 M H_2SO_4 at RT and 0.05 M H_2SO_4 at 80–90°C. The K_d values were comparable to those for untreated beads (Table 6). As 0.5 M H_2SO_4 can remove silicon at room temperature and the removal of titanium has no impact on the molybdenum uptake, it has been chosen as the wash solution for large-scale sorbent pretreatment.

Table 6. Molybdenum uptake by using washed and unwashed sorbents.

Samples	K_d values (mL/g)
Unwashed bead	2.5 x 10^5
Washed bead with 0.5 M H_2SO_4	3.0 x 10^5
Washed bead with 0.05 M H_2SO_4	1.9 x 10^5

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The scaling up of the washing experiment from 20 g to 200 g sorbent shows similar results for the removal of silicon and titanium (Figure 8).
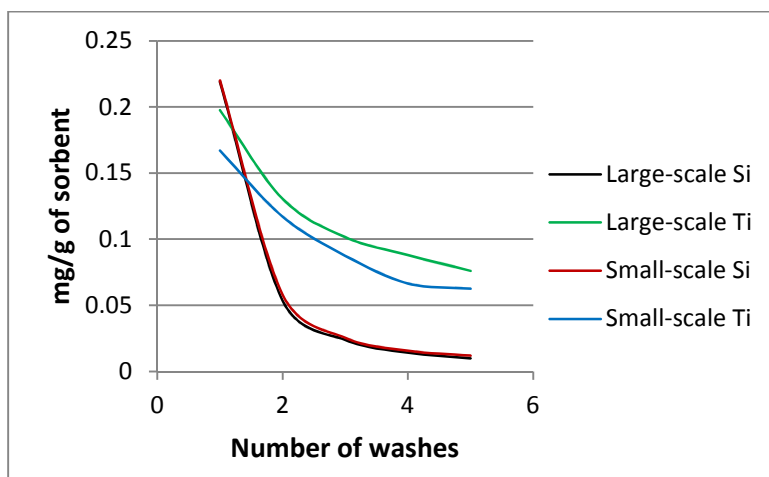
Figure 8. Comparison of small- and large-scale successive washing of TiO_2 sorbents using 0.5 M H_2SO_4. Washing conditions: ratio of beads to solution, 1:5; contact time, 20 min; overhead stirring; temperature, 23°C.

The X-ray fluorescence (XRF) spectra of the washed and unwashed sorbents exhibited similar features. This finding suggests that the washing experiments are not changing the composition of the beads (Figure 9), which could affect their performance.
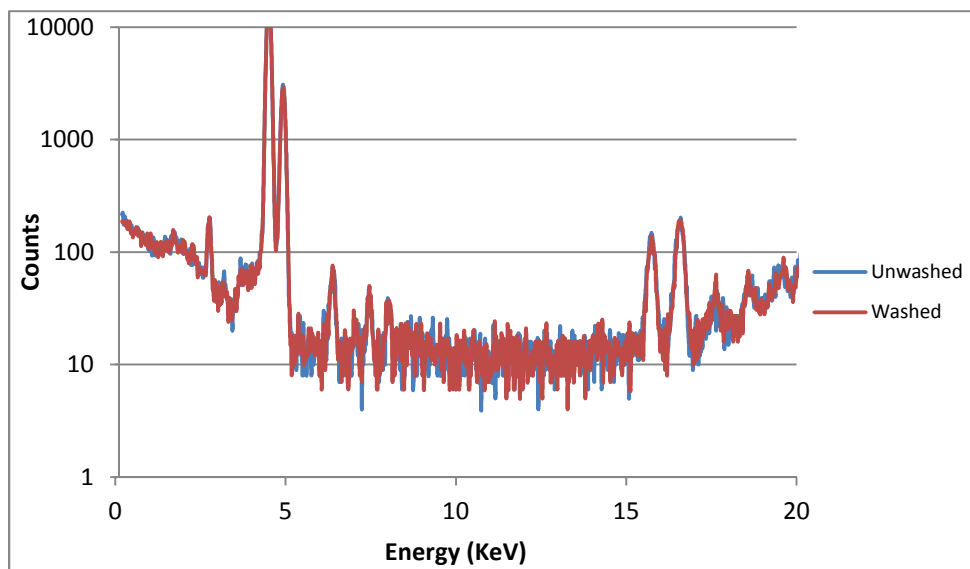
Figure 9. XRF spectra of washed and unwashed beads.

Column testing will be performed with Mo loading from depleted uranyl sulfate and stripping to verify the efficacy of pretreatment. If proven, this pretreatment procedure will be used for the titania sorbent used in phase 2 of the mini-SHINE experiments.

6. REFERENCES

[BERNINGER-1991]. J.A. Berninger, R.D. Whitley, X. Zhang, and N.-H.L. Wang, "A Versatile Model for Simulation of Reaction and Nonequilibrium Dynamics in Multicomponent Fixed-Bed Adsorption Processes," Comput. Chem. Eng. 15:749 (1991).

[CESTAU-2006]. D. Cestau, R. Bavaro, M. Bronca, R. Centurión, A. Novello, P.R. Cristini, J.A. Cestau, and E. Carranza, "Production of Iodine-131 from Low Enriched Uranium Targets," RERTR, Cape Town, South Africa (2006).

[CHEMERISOV-2011]. S. Chemerisov, A.J. Youker, A. Hebden, N. Smith, P. Tkac, C.D. Jonah, J. Bailey, V. Makarashvili, B. Micklich, M. Kalensky, and G.F. Vandegrift, "Development of the Mini-SHINE/MIPS experiments," Proceedings of the Molybdenum-99 Topical Meeting, Santa Fe, New Mexico, December 4–7, 2011, http://mo99.ne.anl.gov/2011/pdfs/Mo99%202011% 20Web%20Papers/S11-P2_Chemerisov-Paper.pdf.

[CHUNG-2010]. P.-L. Chung, J.G. Bugayong, C.Y. Chin, and N.-H.L. Wang, "A Parallel Pore and Surface Diffusion Model for Predicting the Adsorption and Elution Profiles of Lispro Insulin and Two Impurities in Gradient-Elution Reversed Phase Chromatography," J. Chromatogr. A 1217 (45): 7100–7108 (2010).

[MA-1996]. Z. Ma, R.D. Whitley, and N.-H.L. Wang, "Pore and Surface Diffusion in Multicomponent Adsorption and Liquid Chromatography Systems," AIChE J., 42 (5): 1244–1262 (1996).

[ROTSCH-2014]. D.A. Rotsch, A.J. Youker, P. Tkac, D.C. Stepinski, J.F. Krebs, V. Makarashvili, M. Kalensky, Z. Sun, T.A. Heltemes, J.F. Schneider, A.S. Hebden, J.P. Byrnes, L. Hafenrichter, K.A. Wesolowski, S.D. Chemerisov, and G.F. Vandegrift, "Chemical Processing of Mini-SHINE Target Solutions for Recovery and Purification of Mo-99," Topical Meeting on Molybdenum-99 Technological Development, Washington D. C. June 24–27, 2014, http://mo99.ne.anl.gov/2014/pdfs/papers/S9P8%20Paper%20Rotsch.pdf.

[STEPINSKI-2012A]. D.C. Stepinski, D.C., A.J. Youker, and G.F. Vandegrift, Plant-Scale Concentration Column Designs for SHINE Target Solution, ANL/CSE-13/24, Argonne National Laboratory (September 28, 2012). Available at http://www.ipd.anl.gov/anlpubs/2013/10/76978.pdf.

[STEPINSKI-2012B]. D.C. Stepinski and G.F. Vandegrift, Plant-scale Concentration Column Designs for SHINE Target Solution Utilizing AG 1 Anion Exchange Resin, ANL/NE-15/31, Argonne National Laboratory (September 30, 2012). Available at http://www.ipd.anl.gov/anlpubs/2015/11/122761.pdf.

[STEPINSKI-2013]. D.C. Stepinski, J.F. Krebs, M.J. Youker, A.S. Hebden, and G.F. Vandegrift, Documenting Dual-Column Experiment with Mini-SHINE Solution, Argonne National Laboratory, ANL/CSE-13/46, September 30, 2013, http://www.ipd.anl.gov/anlpubs/2014/04/78306.pdf.

[TSUI-2012]. H.-W. Tsui, M.Y. Hwang, L. Ling , E.I. Franses, and N.-H.L. Wang, "Retention Models and Interaction Mechanisms of Acetone and Other Carbonyl-containing Molecules with Amylose tris[(S)-α-methylbenzylcarbamate] Sorbent," J. Chromatogr. A, 1279: 36–48 (2012).

[VAN COTT-1991]. K.E. Van Cott, R.D. Whitley, and N.-H.L. Wang, "Effects of Temperature and Flow Rate on Frontal and Elution Chromatography of Aggregating Systems," Sep. Technol. 1: 142–152 (1991).

[WHITLEY-1993]. R.D. Whitley, K.E. Van Cott, and N.-H.L. Wang, "Analysis of Nonequilibrium Adsorption/Desorption Kinetics and Implications for Analytical and Preparative Chromatography," I&EC Research 32: 149–159 (1993).

[WHITLEY-1994]. R. Whitley X. Zhang, and N.-H.L. Wang, "Protein Denaturation in Nonlinear Isocratic and Gradient Elution Chromatography," AIChE J. 40: 1067–1081 (1994).

[YOUKER-2012]. A.J. Youker, D.C. Stepinski, L. Ling, P.L. Chung, and G.F. Vandegrift, 2012, Plant-Scale Column Designs for SHINE Target Solutions, ANL/CSE-14/24, Argonne National Laboratory (June 29, 2012). Available at http://www.ipd.anl.gov/anlpubs/2014/10/108041.pdf.

[YU-2006]. C.-M. Yu, S. Mun, and N.-H.L. Wang, "Theoretical Analysis of the Effects of Reversible Dimerization in Size Exclusion Chromatography," J. Chromatogr. A, 1132: 99–108 (2006).

APPENDIX A: MINI-SHINE RESULTS

Gamma counting results for the titania extraction column are shown in Tables A-1 and A-2. Table A-1 shows the activities for the feed, column effluent, and acid wash samples (in units of (μCi/g) along with corresponding 1 sigma values. Table A-2 shows the activities for the feed, 1 M sodium hydroxide wash, and 0.1 M sodium hydroxide strip samples (in units of μCi/g) along with corresponding 1 sigma values. To better detect Mo-99 activity in the column effluent and acid wash, it is assumed that transient equilibrium has occurred during gamma counting of all samples, so the half-life of Mo-99 (65.9 h) was used as the half-life for Tc-99m. Due to its short half-life, I-132 was tracked with the half-life of its parent, Te-132. Also tracked was Nb-97 via its parent, Zr-97. Thus, the adsorption and elution behaviors of Tc-99m, I-132, and Nb-97 are representative of the parent's behaviors. The majority of Zr-95 and Mo-99 remain adsorbed on the extraction column. Most of the Mo-99 was recovered during the sodium hydroxide wash and strip steps, but most of the Zr-95 remained adsorbed on the titania column. It is difficult to quantify how much of each isotope was adsorbed on the column and/or was present in the different streams because these samples were collected at a specified period of time and may not accurately represent the concentration in the entire stream collected, i.e., every 30 minutes for the column effluent (CE). Additionally, there may have been cross contamination and/or poor mixing, especially in the feed sample, because the Mo-99 activity in the feed for the extraction column was 96 mCi, and the feed for the concentration column contained 110 mCi.

Gamma counting results for the concentration column (CC) and the final product (purified use in the LMC process [ROTSCH-2014]) are shown in Table A-3. Provided within the table are the decay-corrected data for the feed, eluent, NaOH wash, water wash, CC product (RW1, feed for LMC), and the LMC final purified product (all in units of mCi/g) along with the corresponding 1 sigma values. The activities provided for Tc-99m, I-132, and Nb-97 were handled in the manner described above for the extraction column results. All samples were decay corrected to 12/10/2015 at 8:15:00 AM. The final product except for Ru-103 met all specification criteria.

Table A-1. Gamma counting results for the feed, column effluent, and acid wash samples.

Radionuclide	Feed (µCi/g)	CE#1 (µCi/g)	CE#2 (µCi/g)	CE#3 (vCi/g)	CE#4 (µCi/g)	AW#1 (µCi/g)	AW#2 (µCi/g)	AW#3 (µCi/g)	AW#4 (µCi/g)
	1σ (%)	1σ (%)	1σ (%)	1σ (%)	1σ (%)	1σ (%)	1σ (%)	1σ (%)	1σ (%)
Zr-95	1.22	<0.0051	0.0056	<0.0080	<0.0084	<0.0070	<0.0070	<0.0039	<0.0013
	2.06		29.4						
Nb-95[1]									
U-237	4.06	1.21	1.86	2.79	2.43	1.82	0.39	0.17	0.08
	5.32	5.39	5.42	5.26	5.29	5.58	7.53	15.4	27.5
Eu-156	<0.057	<0.047	<0.045	<0.054	<0.076	<0.059	<0.050	<0.027	<0.0084
Cs-137	0.16	0.070	0.075	0.13	0.14	0.08	0.03	0.0091	<0.0041
	3.63	3.89	3.82	3.61	3.61	4.05	6.91	15.2	
Np-239	30.24	12.9	13.9	26.7	26.1	14.6	4.98	1.27	1.04
	3.94	4.07	4.00	3.94	3.95	4.14	5.00	10.9	11.8
Mo-99	15.22	<0.44	<0.47	0.72	<0.66	<0.71	<0.23	<0.28	<0.53
	3.06			26.7					
Ru-103	4.57	1.63	1.78	2.85	2.96	2.15	1.54	1.25	1.08
	1.87	1.88	1.87	1.87	1.87	1.88	1.90	1.91	1.91
I-132[2]	9.87	3.93	4.92	5.25	6.13	8.69	10.4	9.17	7.26
	3.32	3.60	3.42	3.30	3.59	3.34	3.27	3.26	3.33
Te-131m	3.44	2.04	1.36	1.81	2.28	3.48	4.25	3.41	3.27
	16.12	18.6	28.0	20.0	17.0	18.4	13.2	13.2	13.16
I-131	1.38	0.17	0.16	0.23	0.23	0.27	0.28	0.26	0.20
	3.89	15.3	16.4	15.4	16.6	15.9	12.6	11.4	13.0
I-133	<2.53	<1.54	<1.61	<2.37	<2.47	10.2	5.35	3.91	2.09
						6.46	11.1	17.6	22.0
Cs-136	0.018	<0.011	<0.011	<0.017	<0.018	<0.015	<0.011	<0.0055	<0.0047
	16.29								
Ba-140	2.41	1.51	1.71	4.22	4.09	3.27	1.38	0.36	<0.25
	7.04	6.89	6.29	4.19	4.53	5.07	10.1	21.4	
La-140[1]									
Ce-143	29.5	12.7	13.9	26.1	26.3	15.1	5.61	1.64	1.43
	2.89	3.12	3.07	2.92	2.96	3.43	5.22	12.2	14.2
Zr-97	44.5	<2.25	<2.20	<2.56	<2.50	<3.23	<3.55	<3.03	<2.36
	4.55								

Table A-1. (Cont.)

Radionuclide	Feed (µCi/g) 1σ (%)	CE#1 (µCi/g) 1σ (%)	CE#2 (µCi/g) 1σ (%)	CE#3 (vCi/g) 1σ (%)	CE#4 (µCi/g) 1σ (%)	AW#1 (µCi/g) 1σ (%)	AW#2 (µCi/g) 1σ (%)	AW#3 (µCi/g) 1σ (%)	AW#4 (µCi/g) 1σ (%)
Sr 92	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Tc-99m[2]	15.5 3.31	<0.03	<0.031	<0.042	<0.045	<0.039	<0.047	<0.029	<0.026
Te-132	10.9 5.23	4.42 5.25	5.44 5.31	6.35 5.38	6.63 5.24	9.13 5.15	11.2 5.19	10.2 5.20	8.19 5.24
Nb-97[2]	48.7 4.16	<2.27	<2.36	<3.40	<4.54	<4.36	<3.07	<2.73	<3.19
Rh-105	9.95 4.81	4.49 5.72	4.67 5.72	8.70 4.87	9.52 4.81	4.32 9.37	2.38 11.0	1.27 18.9	1.31 22.3
Sn-125	<0.11	<0.055	<0.082	<0.093	<0.11	<0.10	<0.072	<0.058	<0.040
Sb-127	0.41 7.23	0.080 13.9	0.10 9.29	0.16 12.5	0.16 11.79	0.087 20.8	<0.035	<0.030	<0.027
Sr-91	>12 Half-lives[3]	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Nd-147	3.29 3.67	1.46 3.73	1.52 3.74	2.85 3.64	2.83 3.65	1.67 3.75	0.67 3.99	0.14 10.1	0.071 12.1
Pm-151	2.03 27.8	1.43 24.0	1.67 20.5	2.12 24.2	3.09 18.0	<1.59	<1.40	<0.93	<1.02
Y 93	0.46 13.8	0.27 17.6	0.24 15.5	0.54 10.2	0.38 11.1	0.35 14.7	0.14 29.5	<0.11	<0.10
I-135	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives

[1] Daughter isotope whose activity at EOB could not be accurately calculated from counting data.

[2] Daughter isotope whose activity at time of counting is indicative of mother's behavior.

[3] Indicates more than 12 half-lives have passed during gamma counting.

Table A-2. Gamma counting results for the feed, NaOH wash, and strip samples.

Radionuclide	Feed (µCi/g) 1σ (%)	NaOH Wash#1 (µCi/g) 1σ (%)	NaOH Wash#2 (µCi/g) 1σ (%)	Strip#1 (µCi/g) 1σ (%)	Strip#2 (µCi/g) 1σ (%)	Strip#3 (µCi/g) 1σ (%)	Strip#4 (µCi/g) 1σ (%)	Strip#5 (µCi/g) 1σ (%)
Zr-95	1.22	0.043	0.053	0.013	0.0074	0.0034	0.0033	0.0023
	2.06	11.6	2.02	28.0	15.9	11.4	4.06	5.01
Nb-95[1]								
U-237	4.06	<0.18	0.016	<0.17	<0.059	0.019	0.0051	<0.0036
	5.32		18.8			17.5	24.9	
Eu-156	<0.057	<0.049	<0.0037	<0.048	<0.016	<0.0046	<0.0012	<0.00050
Cs-137	0.16	0.013	0.011	<0.011	<0.0022	<0.00060	<0.00017	<0.00015
	3.63	24.7	13.4					
Np-239	30.24	<0.60	0.34	<0.66	<0.23	<0.024	<0.027	<0.017
	3.94		6.25					
Mo-99	15.22	436.2	1.04	322	46.5	5.67	2.06	1.45
	3.06	2.68	3.78	2.69	2.66	2.77	2.79	3.01
Ru-103	4.57	1.39	0.92	1.46	0.84	0.56	0.51	0.43
	1.87	2.08	1.88	1.97	1.91	1.89	1.88	1.88
I-132[2]	9.87	1.02	1.76	<0.41	0.11	0.027	0.012	0.0078
	3.32	13.3	3.18		26.4	22.1	19.7	24.5
Te-131m	3.44	<1.20	0.060	<1.28	<0.51	<0.022	<0.037	<0.035
	16.12		9.54					
I-131	1.38	28.3	0.38	31.7	7.75	1.86	1.00	0.60
	3.89	1.95	2.38	1.98	2.09	1.94	1.91	1.94
I-133	<2.53	495	5.82	546	129	32.3	17.2	10.3
		2.05	2.47	2.0	2.07	1.89	1.94	2.00
Cs-136	0.018	<0.0062	<0.00057	<0.0070	<0.00067	<0.00049	<0.00026	0.00025
	16.29							24.9
Ba-140	2.41	<0.69	0.074	0.86	<0.17	0.067	<0.015	<0.012
	7.04		15.2	29.9		16.8		
La-140[1]								
Ce-143	29.5	<1.24	0.12	<1.07	<0.42	<0.033	<0.042	<0.038
	2.89		13.9					
Zr-97	44.5	<43.28	2.11	<42.6	<10.3	<0.17	<0.47	<0.42
	4.55		7.68					

Table A-2. (Cont.)

Radionuclide	Feed (µCi/g) 1σ (%)	NaOH Wash#1 (µCi/g) 1σ (%)	NaOH Wash#2 (µCi/g) 1σ (%)	Strip#1 (µCi/g) 1σ (%)	Strip#2 (µCi/g) 1σ (%)	Strip#3 (µCi/g) 1σ (%)	Strip#4 (µCi/g) 1σ (%)	Strip#5 (µCi/g) 1σ (%)
Sr 92	>12 Half-lives[3]	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Tc-99m[2]	15.5	443	1.06	327	47.4	6.03	2.10	1.54
	3.31	3.15	3.16	3.15	3.31	3.16	3.16	3.16
Te-132	10.9	1.09	2.30	<0.70	<0.17	<0.19	0.022	<0.011
	5.23	21.3	3.39				18.6	
Nb-97[2]	48.7	<7.76	2.05	<10.4	<2.33	<0.054	<0.14	<0.17
	4.16		7.11					
Rh-105	9.95	3.35	0.51	5.39	1.15	0.21	0.26	0.18
	4.81	28.2	7.64	22.3	24.5	14.8	13.5	15.2
Sn-125	<0.11	<0.14	<0.0044	0.19	0.093	0.033	0.016	0.015
				27.3	22.4	16.7	14.3	14.0
Sb-127	0.41	0.35	0.018	0.60	0.59	0.39	0.41	0.31
	7.23	10.3	9.7	7.21	4.26	3.19	3.15	3.16
Sr-91	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Nd-147	3.29	2.24	0.020	1.08	<0.042	<0.0062	<0.0018	<0.0015
	3.67	4.47	7.45	6.39				
Pm-151	2.03	<3.59	<0.15	<3.97	<1.35	<0.074	<0.12	<0.091
	27.8							
Y 93	0.46	<0.40	<0.013	<0.36	<0.091	<0.023	<0.010	<0.0062
	13.76							
I-135	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives

[1] Daughter isotope whose activity at EOB could not be accurately calculated from counting data.

[2] Daughter isotope who activity at time of counting is indicative of mother's behavior.

[3] Indicates more than 12 half-lives have passed during gamma counting.

Table A-3. Gamma counting results for the feed, NaOH wash, waste, and strip samples from concentration column and final product from LMC.

Radionuclide	Feed (mCi/g) 1σ (%)	Eluent (mCi/g) 1σ (%)	NaOH Wash (mCi/g) 1σ (%)	Water Wash (mCi/g) 1σ (%)	Waste 2 (mCi/g) 1σ (%)	Product (RF1) (mCi/g) 1σ (%)	LMC Product (mCi/g) 1σ (%)
Zr-95	3.12E-02	3.59E-02	8.84E-04	3.82E-03	3.74E-04	1.46E-01	9.90E-04
	20.1	4.9	8.6	3.4	11.7	11.6	26.2
Nb-95	---	---	---	---	---	---	---
	---	---	---	---	---	---	---
U-237	<0.24	<0.02	<3.15E-03	<9.38E-3	<1.13E-03	<3.68E-2	<1.21E-02
	---	---	---	---	---	---	---
Eu-156	<0.10	<1.08E-02	<1.40E-03	4.50E-03	<5.70E-04	<1.45E-02	<7.04E-03
	---	---	---	21.8	---	---	---
Cs-137	<1.29E-02	<2.10E-03	2.29E-04	6.11E-04	<5.64E-05	<2.72E-03	9.02E-04
	---	---	16.3	5.8	---	---	22.9
Np-239	<9.42E-02	<0.11	<1.19E-02	<1.90	<2.98E-03	<0.16	<7.75E-02
	---	---	---	---	---	---	---
Mo-99	1.08E+02	8.34E+01	1.73E+00	<1.68	3.78E-01	2.42E+01	2.21E+01
	2.8	2.7	2.8	---	2.9	2.8	2.7
Ru-103	1.94E+00	9.49E-01	4.38E-02	8.34E-03	2.44E-02	8.00E-01	7.62E-02
	2	1.9	1.9	2.2	1.9	1.9	2.2
I-132	<0.37	1.26E-01	9.00E-03	<0.12	<1.04E-03	1.53E-01	<3.17E-02
		27.2	21.4	---		22.5	---
Te-131m	<1.43	<0.24	1.65E-01	>12 Half-Lives	<9.05E-5	<0.24	6.24E-01
	---	---	25.6	---	---	---	22.3
J-131	1.81E+01	1.82E-01	2.42E-01	3.74E-02	1.54E-01	1.92E+00	<1.84E-02
	2.3	11.2	2.2	15.2	2	2.6	---
J-133	3.00E+02	3.84E+00	4.28E+00	>12 Half-Lives	2.56E+00	3.22E+01	1.63E+00
	2	7	3.1	---	1.9	2.2	22.1
Cs-136	<1.01E-02	<1.39E-03	<5.11E-05	<2.94E-04	<2.38E-05	<8.29E-04	<5.16E-04
	---	---	---	---	---	---	---
BA-140	<0.79	<8.43E-02	<8.92E-03	<1.14E-02	1.19E-02	<0.17	<3.78E-02
	---	---	---	---	13.9	---	---
Sm-156	>12 Half-Lives[3]	>12 Half-Lives	>12 Half-Lives	>12 Half-Lives	>12 Half-Lives	>12 Half-Lives	>12 Half-Lives
	---	---			---	---	---
La-140	---	---	---	---	---	---	---
	---	---	---	---	---	---	---
Ce-143	<0.92	<0.11	<8.75E-01	>12 Half-Lives	<2.15E-03	<0.22	3.49E-01
	---	---			---	---	20.4

Table A-3. (Cont.)

Radionuclide	Feed (mCi/g)	Eluent (mCi/g)	NaOH Wash (mCi/g)	Water Wash (mCi/g)	Waste 2 (mCi/g)	Product (RF1) (mCi/g)	LMC Product (mCi/g)
	1σ (%)	1σ (%)	1σ (%)	1σ (%)	1σ (%)	1σ (%)	1σ (%)
Zr-97	<0.79	3.55E+00	>12 Half-Lives	>12 Half-Lives	<1.14E-02	<3.08	<7.09
	---	11			---	---	---
Sr-92	>12 Half-Lives	>12 Half-Lives	>12 Half-Lives	>12 Half-Lives	>12 Half-Lives	>12 Half-Lives	>12 Half-Lives
	---	11			---	---	---
Tc-99m	1.15E+02	8.57E+01	1.81E+00	<0.14	4.06E-01	2.45E+01	2.24E+01
	3.3	9	3.3		3.2	3.2	3.2
Te-132	1.00E+00	<0.12	<1.02E-02	<1.61	<2.00E-03	<0.13	<5.65E-02
	24.8	---			---	---	---
Nb-97	<4.94	<0.75	>12 Half-Lives	>12 Half-Lives	4.96E-03	8.40E-01	<1.63
	---	---			22.7	3.2	---
Rh-105	<24.24	<0.50	<4.10E-02	>12 Half-Lives	1.80E-02	1.50E-01	<0.20
		---			15.5	7.25	
Sn-125	<3.06E-2	1.29E-01	<4.59E-03	<1.10E-02	<1.23E-03	<5.21E-02	<1.20E-02
	---	16.2			---	---	---
Sb-127	4.30E-01	3.11E-01	1.15E-02	<1.89E-02	1.42E-03	>12 Half-Lives	<3.02E-03
	9.8	10.9	6.6		8	---	---
Sr-91	>12 Half-Lives	>12 Half-Lives	>12 Half-Lives	>12 Half-Lives	5.95E-01	1.90E-01	>12 Half-Lives
					11.9	7.3	
Nd-147	6.56E-01	6.29E-01	<1.65E-03	<2.27E-03	<6.55E-04	8.15E+00	1.07E-01
	10.9	15.6			---	20.8	5.0
Pm-151	<3.26	3.67E-01	<0.11	>12 Half-Lives	<5.78E-03	<6.87E-02	<0.45
	---	3.9			---	---	---
Y-93	<0.49	<6.00E-02	<4.06E-03	<1.00E-02	2.62E-03	<7.81E-02	<1.90E-02
	---	---			---	---	---
J-135	>12 Half-Lives	>12 Half-Lives	>12 Half-Lives	>12 Half-Lives	>12 Half-Lives	>12 Half-Lives	>12 Half-Lives
	---	---			---	---	---

[1] Daughter isotope whose activity at EOB could not be accurately calculated from counting data.

[2] Daughter isotope who activity at time of counting is indicative of mother's behavior.

[3] Indicates more than 12 half-lives have passed during gamma counting.

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